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TITLE OF THE INVENTION

COLD STORAGE AGENT, COLD INSULATING MATERIAL, AND FREEZER

Inserted: COLD PRESERVING MATERIAL

BACKGROUND OF THE INVENTION

5 Field of the Invention

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The present invention relates to a cold storage agent, a cold insulating material, and a freezer. In the present invention, the cold insulating material means a material obtained by dissolving the cold storage agent according to the present invention in water, and freezing the aqueous solution of the cold storage agent in a container. The freezer according to the present invention includes a freezing case and a transport container.

Description of Prior Art

As for a freezing mixture, a combination of NH_4Cl and KNO_3 , a combination of $NaNO_3$ and NH_4NO_3 , or a combination of KNO_3 and NH_4SCN is known. However, a cold storage agent which can be used as a substitute for dry ice, that is, a cold storage agent which can provide temperatures optimum for freezing (-35 to -50°C) has not yet been found.

SUMMARY OF THE INVENTION

The present invention provides a cold storage agent comprised of a combination of two kinds of salts capable of providing a lower temperature as compared with a cold storage agent comprised of a single salt, and a cold

Inserted: cold preserving
material

Inserted: cold preserving
material

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material

insulating material obtained by dissolving such a cold storage agent in water, and freezing the aqueous solution of the cold storage agent in a container made of polyethylene or the like and having a thickness of 1 to 3 mm. More specifically, the present invention provides a cold storage agent comprised of a combination of salts capable of obtaining a cold storage effect of maintaining a low temperature of -35°C or lower, and a cold insulating material prepared using such a cold storage agent. Further, the present invention provides a freezer which contains

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material

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the present invention provides a freezer which contains such a cold insulating material capable of providing a low temperature of -35° C or lower, and can maintain the temperature of the inside thereof at -20° C or lower.

The present inventor has prepared an aqueous solution of the cold storage agent comprised of a combination of at least two salts composed of identical negative ions and different positive ions. An example of a negative ion includes chloride ion, sulfate ion, or nitrate ion. The salt may be a monovalent salt or a bivalent salt. In the case of a monovalent salt, an example of a positive ion includes sodium ion, potassium ion, or ammonium ion. In the case of a bivalent salt, an example of a positive ion includes magnesium ion or calcium ion.

In two salts, negative ions should be identical, and a combination of positive ions should be a combination of monovalent ion and monovalent ion, or a combination of bivalent ion and bivalent ion. That is, the cold storage

agent of the present invention is comprised of a combination of a salt composed of a monovalent negative ion and a monovalent positive ion and a salt composed of a monovalent negative ion and a monovalent positive ion. A combination of a salt composed of a monovalent negative ion and a monovalent positive ion and a salt composed of a monovalent negative ion and a bivalent positive ion should be excluded.

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As described above, in the present invention, an example of a negative ion includes chloride ion, sulfate ion, or nitrate ion. Among them, chloride ion (Cl⁻) is preferable because it has been confirmed from experimental results that chloride ion has the effect of markedly lowering melting point and prolonging cold storage duration.

As for a positive ion, in the case of a monovalent salt, sodium ion (Na_), potassium ion (K_), or ammonium ion (NH₄_) can be mentioned. In the case of a bivalent salt, magnesium ion (Mg²⁺) or calcium ion (Ca²⁺) is preferable.

Accordingly, in the present invention, a preferred example of a combination of monovalent salts includes a combination of NaCl and KCl, a combination of NaCl and NH $_4$ Cl, a combination of KCl and NH $_4$ Cl, or a combination of NaCl, KCl and NH $_4$ Cl. As for a combination of bivalent salts as chloride, a combination of MgCl $_2$ and CaCl $_2$ can be mentioned.

Among bivalent salts, a combination of a bivalent salt composed of chloride ion as a negative ion and calcium

Inserted: Na+

Inserted: NH4+

ion as a positive ion and a bivalent salt composed of chloride ion as a negative ion and magnesium ion as a positive ion is preferable in terms of lowering of melting point and prolongation of cold storage duration as compared with a single chloride salt. Further, such combined bivalent salts can provide a low temperature of -37°C (in the case of a combination of magnesium chloride as a main component and calcium chloride) or -45°C (in the case of a combination of calcium chloride as a main component and magnesium chloride), and therefore a cold storage agent comprised of such combined bivalent salts can be used as a substitute for dry ice.

Furthermore, a freezer or a transport container capable of maintaining the temperature of the inside thereof at a low temperature of -20°C or lower for a long period of time can be achieved by setting a cold-insulating Inserted: cold preserving material obtained by freezing such a cold storage agent of material the present invention in an accommodation member, in the inside of the freezer. Since such a cold insulating Inserted: cold preserving material can maintain the temperature of the inside of the material freezer at -20°C or lower for a long period of time, it can be suitably used for freezing food, as a substitute for dry Inserted: cold preserving ice. The cold insulating material is preferably set in the material upper portion of the freezer, but it is not always Inserted: cold preserving necessary to set the cold insulating material in the upper material

portion of the freezer as long as air in the freezer is

stirred by using a fan.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph which provides a comparison of a change in surface temperature between a cold insulating material according to the present invention and a conventional cold-insulating material; and

Inserted: cold preserving <u>material</u>

Inserted: cold preserving material

FIG. 2 is a schematic illustration which shows the inside of a freezer containing the cold insulating material according to the present invention.

Inserted: cold preserving material

DETAILED DESCRIPTION OF THE INVENTION

Hereinbelow, a description will be made with regard to embodiments of the present invention.

1/2 to 1/10, preferably, 1/3 to 1/5 wt% of ammonium chloride (NH4Cl) is added with respect to 1 wt% of sodium chloride (NaCl) or potassium chloride (KCl). Alternatively, 1/3 to 1/5 wt% of sodium chloride (NaCl) or potassium chloride (KCl) may be added with respect to 1 wt% of ammonium chloride (NH₄Cl).

Inserted: Here, wt% means the weight percentage of salt dissolved in water (salt weight g in 100g solution).

The basic concept regarding the above case is as follows- 1/3 to 1/5 wt% of a main component is reduced from an optimum amount (wt%) of the main component when used singly, and the reduced amount (1/3 to 1/5 wt%) of the main component is added to another salt. In this case, the total amount of the main component is substantially the same as the optimum amount (wt%). Alternatively, -1/3 to 1/5 wt% of the optimum amount of the main component whenused singly may be added to another salt.

Inserted: "with respect to"

Inserted:

Inserted: amount (

Inserted:)

Inserted: another salt

Inserted: by 1/3 to 1/5 amount (wt%).

Inserted: another salt is

Inserted: by 1/3 to 1/5 amount (wt%)

Inserted: the optimum amount of main component

Inserted: , wherein the
total amount is increased by 1/3 to 1/5 (wt%)

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It is also possible to obtain a preferable result by reducing 1/3 to 1/5 wt% of the main component (sodium chloride (NaCl) or potassium chloride (KCl)), and adding ammonium chloride (NH4Cl) as much as the above reduced amount so that the total amount of the respectivecomponents becomes substantially the same as the amount of the main component before reduction. The same thing can be said for the case of a combination of bivalent salts (magnesium chloride (MgCl₂) and calcium chloride (CaCl₂)). For example, $\frac{1}{2}$ to $\frac{1}{8}$ wt% of calcium chloride (CaCl₂) is added with respect to 1 wt% of magnesium chloride (MgCl2). Alternatively, 2 to 8 wt% of calcium chloride (CaCl₂) may be added with respect to 20 wt% of magnesium chloride (MgCl₂) that is an optimum amount of magnesium chloride when used singly. It is preferred that the weight percentage of the main component is in the range of 10 to 25. The thus obtained cold storage agent is dissolved in water to prepare an aqueous solution thereof, and the prepared aqueous solution is placed in a container made of polyethylene or the like and then frozen, to obtain a coldinsulating material.

In the present invention, the cold insulating material obtained by dissolving a mixture of magnesium chloride (MgCl₂) as a main component and calcium chloride (CaCl₂) in water and freezing the aqueous solution of the mixture can maintain a low temperature of -36° C and has a longer cold storage duration as compared with a cold—

Inserted: by 1/2 to 1/8 amount (wt%) to the optimum amount of

Inserted: reducing magnesium chloride (MgCl2) by 1/2 to 1/8 amount (wt%), and adding calcium chloride (CaCl2) by 1/2 to 1/8 amount (wt%).

Inserted: ¶

inserted: dissolved in
water

Inserted: cold preserving
material

Inserted: cold preserving
material

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insulating material comprised of magnesium chloride (MgCl₂) alone. On the other hand, the cold insulating material comprised of a mixture of calcium chloride (CaCl₂) as a main component and magnesium chloride (MgCl₂) can provide a lower temperature of -45°C. Therefore, such a cold—insulating material obtained by freezing the cold storage agent of the present invention in a container can be used as a substitute for dry ice. Further, the cold insulating—material obtained by dissolving a mixture of sodium

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Inserted: cold preserving material

Inserted: cold preserving material

Inserted: cold preserving
material

Inserted: cold preserving
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chloride (NaCl) as a main component (having a melting point of -20°C when used singly) and ammonium chloride (NH₄Cl) in water, and freezing the aqueous solution of the mixture has a lower melting point of -25°C and a long cold storage duration (see FIG. 1). As described above, such a mixed cold storage agent (cold insulating material) has an excellent cold storage effect as compared with a cold storage agent (cold insulating material) comprised of a single component.

Inserted: cold preserving
material

Inserted: cold preserving
material

FIG. 2 is a schematic illustration which shows the inside of the freezer containing the cold insulating material according to the present invention. As shown in FIG. 2, a cold insulating material 12 obtained by freezing the cold storage agent dissolved in water contained in an accommodation member is placed inside a freezer 10. A transport container is also included in such a freezer. The cold insulating material is placed in the upper portion of the freezer, and therefore, a storage part 14 for

Inserted: cold preserving
material

Inserted: cold preserving
material

Inserted: cold preserving
material

setting the cold insulating material is provided in the upper portion of the freezer. The freezer may have a fan 16 for uniformly filling the inside of the freezer with cold air generated by the cold insulating material placed in the storage part 14, and further a cold air blowing means 18 for blowing cold air generated by the cold insulating material placed in the upper portion of the freezer in the downward direction.

Inserted: cold preserving
material

Inserted: cold preserving
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Inserted: cold preserving material

Example 1

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Each of a 23 wt% aqueous sodium chloride solution and an aqueous solution containing 17 wt% of sodium chloride and 5 wt% of ammonium chloride was placed in a container made of polyethylene and having a thickness of 1 mm, and then frozen. Thereafter, the melting point of each of the frozen aqueous solutions was measured, and the former was -20°C and the latter was -25°C. These frozen

Each of a 20 wt% aqueous potassium chloride

aqueous solutions had the same cold storage duration.

Example 2

solution and an aqueous solution containing 15 wt% of potassium chloride and 5 wt% of ammonium chloride was placed in a container made of polyethylene and having a thickness of 1 mm, and then frozen. Thereafter, the melting point of each of the frozen aqueous solutions was measured, and the former was -10.5°C and the latter was -17°C. These frozen aqueous solutions had the same cold storage duration.

Inserted:_,

Inserted:_,

Example 3

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Each of a 20 wt% aqueous ammonium chloride solution and an aqueous solution containing 20 wt% of ammonium chloride and 5 wt% of potassium chloride was placed in a container made of polyethylene and having a thickness of 1 mm, and then frozen. Thereafter, the melting point of each of the frozen aqueous solutions was measured, and the former was -16°C and the latter was -17.5°C. The cold storage duration of the latter was 1.15 times longer than that of the former.

Example 4

| Table 1 | | | | | minutes | | | |
|---|-----|-----|-----|-----|---------|-----|------------|--|
| | 60 | 120 | 180 | 260 | 300 | 360 | 420 | |
| MgCl ₂ 15% | -81 | -31 | -31 | -29 | -23 | -15 | -12 | |
| MgCl ₂ 15 + CaCl ₂ 5% | -42 | -40 | -36 | -33 | -26 | -16 | - 5 | |
| MgCl ₂ 15 + CaCl ₂ 2.5% | -42 | -34 | -32 | -30 | -24 | -15 | -12 | |
| MgCl ₂ 20 + CaCl ₂ 7.5% | -45 | -37 | -34 | -29 | -18 | -8 | -3 | |
| MgCl ₂ 20 + CaCl ₂ 2.5% | -35 | -34 | -33 | -30 | -20 | -7 | -3 | |

A 15 wt% aqueous magnesium chloride solution, an aqueous solution containing 15 wt% of magnesium chloride and 2.5 wt% of calcium chloride, an aqueous solution containing 15 wt% of magnesium chloride and 5 wt% of calcium chloride, an aqueous solution containing 20 wt% of magnesium chloride and 7.5 wt% of calcium chloride, and an aqueous solution containing 20 wt% of magnesium chloride and 2.5 wt% of calcium chloride were prepared as cold storage agents. Each of the cold storage agents was placed

containing 23 wt% of sodium chloride alone were prepared.

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in a container made of polyethylene and having a thickness of 1 mm and a capacity of 550 mL, and was then frozen. Inserted: cold preserving thus obtained each of the cold insulating materials was material placed in a styrofoam box having a size of 30 \times 21 \times 12 cm and a thickness of 2 cm, and a change in surface inserted: gold preserving temperature of cold insulating material was measured. The material Inserted: cold preserving melting point of each of the cold insulating materials is material shown in Table 1. Inserted: cold preserving The cold insulating material comprised of 15 wt% mate<u>ria</u>l of magnesium chloride alone had a melting point of -31°C. On the other hand, in the case of the cold insulating inserted: cold preserving material comprised of a mixture of magnesium chloride and material Inserted: cold preserving calcium chloride, the cold-insulating material containing <u>material</u> 2.5 wt% of calcium chloride had a lower melting point as Inserted: cold preserving compared with the cold insulating material comprised of material Inserted: cold preserving magnesium chloride alone, and the cold-insulating material material containing 5 wt% or more of calcium chloride had a markedly lowered melting point. Further, the cold insulating-Inserted: cold preserving material containing 20 wt% of magnesium chloride had a material still lower melting point. Inserted: cold preserving Moreover, (a) a cold insulating material material containing 15 wt% of magnesium chloride and 5 wt% of Inserted: cold preserving calcium chloride, (b) a cold insulating material containing material 15 wt% of magnesium chloride alone, (c) a cold-insulating-Inserted: cold preserving material containing 17 wt% of sodium chloride and 5 wt% of <u>materi</u>al Inserted: cold preserving ammonium chloride, and (d) a cold insulating material material

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Inserted: cold preserving For each of the cold insulating materials, a change in material **Inserted:** çold preserving surface temperature of cold insulating material when two material **Inserted:** cold preserving blocks of the cold-insulating material were placed in a material freezer was measured. The result is shown in FIG. 1, Inserted: cold preserving wherein $\triangle - \triangle$ represents the cold insulating material (a), \blacklozenge material Inserted: cold preserving ullet represents the cold insulating material (b), Δ - Δ <u>materia</u>l Inserted: cold preserving represents the cold insulating material (c), and $\Diamond - \Diamond$ material represents the cold insulating material (d). As shown in Inserted: cold preserving material FIG. 1, the cold insulating material comprised of a mixture Inserted: cold preserving material of chloride salts showed a lower temperature as compared Inserted: cold preserving with the cold insulating material comprised of a single material chloride salt, and there was no difference in change in surface temperature with the passage of time between them. Inserted: cold_preserving Specifically, the cold insulating-material comprised of a material mixture of magnesium chloride and calcium chloride (a) showed a lower temperature as compared with the cold-Inserted: cold preserving insulating material comprised of magnesium chloride alone material Inserted: cold preserving (b). Similarly, the cold insulating material comprised of material a mixture of sodium chloride and ammonium chloride (c) showed a lower temperature as compared with the cold-Inserted: cold preserving insulating material comprised of sodium chloride alone (d). material In addition, there was no difference in change in surface temperature with the passage of time between them. Example 5 Inserted: cold preserving A cold insulating material comprised of 10 wt% of material potassium chloride alone had a melting point of -11°C. inserted: cold preserving the other hand, a cold insulating material comprised of a

material

mixture of 10 wt% of potassium chloride and 3 wt% of ammonium chloride had a melting point of -13° C.

Example 6

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A cold insulating material comprised of 15 to 17

Inserted: cold preserving material

On the other hand, a cold insulating material comprised of

wt% of calcium chloride alone had a melting point of -44°C.

Inserted: cold preserving
material

a mixture of 15 wt% of calcium chloride and 5 wt% of magnesium chloride had a melting point of -47.5° C.

WHAT IS CLAIMED IS:

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- 1. A cold storage agent comprising a combination of two salts composed of identical negative ions and different positive ions having the same valence, the valence being monovalence or bivalence.
- 2. The cold storage agent as claimed in claim 1, wherein the monovalent positive ion is one of sodium ion, potassium ion and ammonium ion, and the negative ion is chloride ion.
- 3. The cold storage agent as claimed in claim 1, wherein the bivalent positive ion is one of magnesium ion and calcium ion, and the negative ion is chloride ion.

4. The cold storage agent as claimed in any one of claims 1 to 3, wherein the concentration of a main component is in the range of 10 to 25 wt%.

Inserted: dissolved in
water

- 5. The cold storage agent as claimed in claim 4, wherein the cold storage agent is obtained by mixing sodium chloride or potassium chloride as a main component and ammonium chloride, wherein 1/2 to 1/10, preferably, 1/3 to 1/5 wt% of ammonium chloride is added with respect to 1 wt% of sodium chloride or potassium chloride.
 - 6. The cold storage agent as claimed in claim 4,

wherein the cold storage agent is obtained by mixing ammonium chloride as a main component and sodium chloride or potassium chloride, wherein 1/3 to 1/5 wt% of sodium chloride or potassium chloride is added with respect to 1 wt% of ammonium chloride.

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7. The cold storage agent as claimed in claim 4, wherein the cold storage agent is obtained by mixing magnesium chloride as a main component and calcium chloride in an amount of 1/2 to 1/8 wt% of the amount (wt%) of the main component.

Inserted: , wherein

Inserted: calcium chloride
is added with respect to
1 wt% of magnesium
chloride.

8. The cold storage agent as claimed in claim 4, wherein the cold storage agent is obtained by mixing magnesium chloride as a main component and 2 to 8 wt% of calcium chloride.

Inserted: calcium

Inserted: magnesium
chloride, wherein 1/

Inserted: 1/

Inserted: magnesium

Inserted: is added with respect to 1 wt% of calcium chloride

freezing the cold storage agent as claimed in claim 1 dissolved in water contained in an accommodation member.

9. A cold-insulating material obtained by

Inserted: cold preserving
material

10. A freezer which contains a cold insulating material obtained by freezing the cold storage agent as claimed in claim 1 dissolved in water contained in an accommodation member in the inside thereof.

Inserted: cold preserving
material

11. The freezer as claimed in claim 10, wherein

the freezer is a container.

12. The freezer as claimed in claim 10 or 11, further comprising a fan in the inside thereof.

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13. The freezer as claimed in claim 12, wherein the eold insulating material is provided in the upper portion thereof.

Inserted: cold preserving
material

10 14. Th

14. The freezer as claimed in claim 13, further comprising a cold air blowing means for blowing cold air generated by the cold insulating material provided in the upper portion thereof in the downward direction.

inserted: cold preserving
material

ABSTRACT OF THE DISCLOSURE

A cold insulating material capable of maintaining material the temperature of the inside of a freezer at -20°C or lower for a long period of time is provided. Such a cold insulating material is obtained by freezing a mixture of material sodium chloride and potassium chloride dissolved in water or a mixture of magnesium chloride and calcium chloride dissolved in water.